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EVALUATION OF THE REMOBILIZATION POTENTIAL  
OF TECHNETIUM AND URANIUM ASSOCIATED  
WITH SLUDGE IN THE S-3 PONDS  
AT THE Y-12 PLANT

**MARTIN MARIETTA**

April 1987

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for

Environmental Management Department  
Health, Safety, Environment  
and Accountability Division

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**Internal Correspondence****MARTIN MARIETTA ENERGY SYSTEMS, INC.****December 30, 1985****TO: Distribution****FROM: S. Y. Lee and L. K. Hyder**

**SUBJECT: EVALUATION OF THE REMOBILIZATION POTENTIAL OF TECHNETIUM AND  
URANIUM ASSOCIATED WITH SLUDGE IN THE S-3 PONDS AT THE Y-12 PLANT.**

**SUMMARY**

The sample (953129) collected from the Southeast basin of the S-3 Ponds at the Y-12 Plant was characterized to evaluate the remobilization potential of technetium-99 (Tc) and uranium-234,235,238 (U) under controlled acidic conditions in the laboratory. The treatments included: (1) successive water and acetic acid leaching at equilibrium pHs of 11.6, 8.1, and 2.8 and (2) hydrochloric acid titration to pH 2 with restoration to alkaline conditions (pH 11) by sodium hydroxide titration. The sample as received consisted of 34 % interstitial water and 66 % solid (wet weight base), which is termed "sludge" in this report. The interstitial water contained 3800 Bq/kg of Tc and 6 Bq/kg of U, while the sludge had 82,000 Bq/kg of Tc and 24,100 Bq/kg of U.

The results showed that the water washes removed only 5.4 % of the Tc and less than 0.1 % of the U associated with the sludge, while removing 9.5 % of the sludge weight. The first acetic acid leaching at pH 8.1 removed 6.3 % of the Tc, 5.1 % of the U, and 31 % by weight of the sludge. The second acetic acid leaching at pH 2.8 removed 24.7 % of the Tc, 89.5 % of the U, and 45.7 % by weight of the sludge. The remaining insoluble residue (13.8 % by weight) contained 63.6 % of the total Tc and 5 % of the total U in the sludge. Hydrochloric acid titration with end point at pH 2

released 9.2 % of Tc and 73 % of U. Reverse titration with sodium hydroxide to pH 11 reprecipitated most of the U released, but also resulted in the release of additional Tc from the sludge, rather than its reprecipitation from solution.

The compositions of the leachates from the successive treatments indicate that most of the Tc is incorporated in iron and sulfide compounds  $[(\text{Fe}, \text{Tc})_2\text{O}_3]$ , and  $\text{Tc}_2\text{S}_7$ , while the U is in iron and aluminum oxyhydroxide compounds  $[(\text{Fe}, \text{Al}, \text{U})_2\text{O}_3]$  and  $(\text{Al}, \text{Fe}, \text{U})(\text{OH})_3$ . The iron and aluminum compounds containing Tc or U are soluble in acidic (pH <5) solutions, but the technetium sulfide compounds are insoluble in acid solutions.

From the immediate waste management viewpoint, the remobilization potential of Tc and U in the sludge is low, as long as proposed containment methods are able to isolate the sludge from the intrusion of complexing organics, acids, and chemical oxidants. In the long term, however, unless the containment method can provide complete hydrologic isolation, contact with weakly acidic soil solutions and groundwaters could result in a significant volume reduction of the sludge through gradual dissolution of carbonate constituents. This volume reduction may induce structural instability in the containment, which will necessitate continuing maintenance of the facility. These predictions are based solely on the chemical characteristics of the sludge; other factors such as in situ physical and hydrological characteristics, engineering properties, and cost effectiveness, should also be considered in an ultimate remedial action plan.

## INTRODUCTION

After extensive studies of the hazardous chemical and radionuclide contamination of S-3 pond water at the Y-12 Plant, the pond water was neutralized as a first step toward remedial action. This operation generated considerable amounts of sludge which contained the precipitates of hazardous materials, including the radionuclides technetium-99 and uranium-234,235,238. Since both radionuclides are known to be relatively mobile under selected chemical conditions, chemical characterization of the sludge was requested by the Y-12 Health, Safety, Environment and Accountability Division, in order to develop the second phase of the remedial action program.

The objective of this investigation was to determine the characteristics of technetium and uranium precipitated with the sludge through successive leaching and acid-alkali titration experiments. The experiments are intended to provide information related to the long-term remobilization potential of the radionuclides in the sludge.

## EXPERIMENTAL PROCEDURE

Successive Water and Acetic Acid Leaching: The sludge was agitated on a shaker for approximately 30 min, then 200 ml were transferred to a tared 250 ml glass centrifuge bottle. Sample weight and pH were determined.

To remove water-soluble ions, the sludge sample was centrifuged at 1700 rpm for 10 min. The supernate was decanted and filtered through a

0.45  $\mu$ m Gelman Acrodisc filter apparatus (sample 1). The wet weight of the residue was measured, and from it the weight of the supernate calculated. An aliquot (110 ml) of distilled deionized water was added to the residue, and the mixture agitated for 24 hrs. The suspension was centrifuged at 1700 rpm for 10 min and the supernate decanted and filtered (sample 2). Weights of residue and of supernate were determined as before. The residue was divided into two approximately equal aliquots, and 150 ml of distilled deionized water added to each. These mixtures were treated in the same way as the previous wash (sample 3).

To remove acetate-soluble ions, each of the two residue aliquots was mixed with 100 ml of distilled deionized water, then glacial acetic acid was added dropwise, with stirring, until the pH of each suspension appeared to stabilize at 7 (4 ml of acid to each aliquot). The suspensions were agitated for 24 hrs., followed by pH measurement, centrifugation, and decantation/filtration of supernate (sample 4). The addition of 100 ml of distilled deionized water plus acetic acid to each of the residues was repeated, this time until the pH appeared to stabilize at 5 (9.0 ml of acid for aliquot 1, 10.2 ml for aliquot 2). The wash procedure was as before (sample 5).

The final residues in the centrifuge bottles were combined, oven-dried at 100°C overnight, and weighed. One half gram of the residue plus a sample of untreated sludge were examined by X-ray powder diffractometry for mineral identification. The remainder was leached with a 6% sodium hypochlorite solution at 60°C to oxidize the technetium and uranium present. The residue from this treatment was fused with a mixture of sodium and potassium carbonate salts for complete dissolution (sample 6).

Acid and Alkali Titrations: The sludge sample was agitated on a shaker for 30 min., then four sludge replicates, approximately 20 g each, were transferred to tared 250 ml glass centrifuge bottles and their weights determined.

The four replicates were centrifuged at 1700 rpm for 20 min. and the supernates decanted. The wet weights of the residues were measured, and from them the weights of the supernates calculated.

Thirty ml of distilled deionized water were added to each replicate. The mixtures were agitated for four hours, then centrifuged at 1700 rpm for 20 min. The supernates were decanted; those from replicates 1 and 2 were combined, as were those from replicates 3 and 4. The weights of the residues were measured, and from them the weights of the supernates calculated.

A second water wash was performed in the same manner as the first. Supernates from replicates 1 and 2 were combined with those from the first wash, as were the supernates from replicates 3 and 4. The wet weights of the residues were measured, then the samples were oven-dried overnight at 100° C and weighed again.

Ten ml of distilled deionized water were added to each residue to make a slurry. These were agitated in a shaker for approximately 1 hr., and pHs measured. Hydrochloric acid (2 N HCl) was added dropwise, with stirring, to each replicate until the pHs stabilized at 2. At this point, replicates 1 and 2 were centrifuged at 1700 rpm for 30 min., until the supernates were clear, then decanted. The supernates were held in separate containers for analysis.

Sodium hydroxide (2 N NaOH) was added dropwise, with stirring, to replicates 3 and 4 until the pHs stabilized at 11. The replicates were then centrifuged for 30 min. and decanted as before, the supernates being held in separate containers for analysis. Chemical analyses were performed by the Analytical Chemistry Division of Oak Ridge National Laboratory.

## RESULTS AND DISCUSSION

The sample received from Y-12 was a yellowish brown slurry composed of 34 % interstitial water, separable by centrifugation, and 66 % wet solid which was defined as "sludge" in this report. The interstitial water, sludge, and leachate solutions, together with the dried residue, were analyzed for radionuclides, cations and anions, in order to identify phases readily soluble in the different leaching solutions. The results of chemical analyses of the samples are presented in Tables 1 and 2.

The interstitial water contained a noticeable amount of technetium-99 (Tc) and an insignificant amount of uranium-234,235,238 (U), but the sludge contained considerable amounts of both radionuclides (Table 1). The presence of Tc in the aqueous phase suggests that the pond water had insufficient amounts of dissolved ferrous iron and sulfide to remove Tc by coprecipitation during neutralization of the acidic pond water (Lee and Bondietti 1983a). The interstitial water was saturated with calcium, sodium, and nitrate. X-ray powder diffraction analysis indicated that the solid phase of the nontreated sludge was composed of calcium aluminum sulfate or nitrate hydrate, calcium carbonate hydrate, calcite, anhydrite, one to two unidentified crystalline minerals, and amorphous precipitate.

Table 1. Radioactivity of Unleached Sludge Received from Y-12 (Bq/kg)

	$^{99}\text{Tc}$	$^{234,235,238}\text{U}$
Supernate (pH 11.2)	3800	6.47
Sludge (pH 11.2)	82,000	24,100

Table 2. Dissolved and Residue composition after Successive Leaching

Sample number	Successive leaching treatment					Dry residue
	1	2	3	4	5	6
Equilibrium pH	11.2	11.2	11.6	8.12	2.75	NA <sup>a</sup>
$^{99}\text{Tc}$ (Bq/L)	3800	2100	700	2200	7700	1,800,000 <sup>b</sup>
$^{234}\text{U}$ (Bq/L)	4.3	2.4	1.5	260	4100	30,000 <sup>b</sup>
$^{235}\text{U}$ (Bq/L)	0.6	0.3	0.2	28	610	ND <sup>c</sup>
$^{238}\text{U}$ (Bq/L)	1.6	1.1	0.8	500	7600	37,000 <sup>a</sup>
Ca ( $\mu\text{g/ml}$ )	2490	1390	652	10,400	12,600	ND
Mg ( $\mu\text{g/ml}$ )	0.3	0.2	0.2	49	976	ND
K ( $\mu\text{g/ml}$ )	100	52	11	7	41	ND
Na ( $\mu\text{g/ml}$ )	1700	713	124	25	25	ND
Si ( $\mu\text{g/ml}$ )	0.9	0.5	0.5	0.4	329	ND
Al ( $\mu\text{g/ml}$ )	46	64	83	10	3130	ND
Fe ( $\mu\text{g/ml}$ )	1.7	0.9	0.4	1.5	325	ND
$\text{SO}_4$ ( $\mu\text{g/ml}$ )	100	100	50	1600	1500	ND
$\text{NO}_3$ ( $\mu\text{g/ml}$ )	9700	4300	1900	5900	1900	ND
$\text{HCO}_3$ ( $\mu\text{g/ml}$ )	564	168	0	10,000	8680	ND
Cl ( $\mu\text{g/ml}$ )	490	230	53	62	36	ND

<sup>a</sup> Not applicable

<sup>b</sup> Bq/kg

<sup>c</sup> Not determined

The water washes (samples 2 and 3) removed most of the dissolved components but had little effect on either the pH or the technetium and uranium solubilities in the sludge (Table 2). The residue weights showed relatively little change, while the approximate doubling of leachate volumes resulted in a concomitant reduction of technetium and uranium concentrations. The small sludge weight changes are attributed to the dissolution of readily soluble nitrate compounds.

With the addition of acetic acid, however, the solubilities changed radically. About 31 % and 46 % of the residue were dissolved at equilibrium pHs 8.1 and 2.8, respectively (Table 3). The first acetic acid leaching removed about 6 % of the Tc and 5 % of the U, and the

Table 3. Weight Loss and Removal of Technetium and Uranium  
Successive Leachings

Successive leaching	Percent removed		
	Weight	$^{99}\text{Tc}$	$^{234,235,238}\text{U}$
1st Water Wash (pH 11.2)	7.76	2.92	0.01
2nd Water Wash (pH 11.6)	1.72	2.47	0.02
1st Acetic Acid Wash (pH 8.12)	31.03	6.32	5.13
2nd Acetic Acid Wash (pH 2.75)	45.69	24.74	89.49
Residue	13.79	63.55	5.36

second leaching removed 25 % of the Tc and 89 % of the U in the sludge. Both treatments dissolved large amounts of calcium, carbonate, nitrate, and sulfate, but the second treatment also released considerable amounts of magnesium, silicon, aluminum, and iron.

The composition of the supernate from the second acetic acid treatment indicates that most of the U and about 25 % of the Tc in the sludge were structurally incorporated into iron oxide and/or aluminum hydroxide phases. Dissolved U readily coprecipitates with most dissolved heavy metals during alkali titration, but Tc does so only when the heavy metals are able to reduce the oxidation state of the Tc, e.g., ferrous rather than ferric iron (Lee and Bondietti 1983a and 1983b).

After successive leachings, the remaining residue constituted about 14 wt % of the original sludge and contained quartz, gibbsite, plaster ( $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ) and colloidal iron hydroxide. The residue contained 64 % of the Tc and 5 % of the U in the original sludge (Table 2). The suspected Tc compound in the residue is technetium sulfide ( $\text{Tc}_2\text{S}_7$ ), which is insoluble in acid solutions. Since the chemical environment of the pond water prior to neutralization is not known, this identification is entirely speculative. Nevertheless, the amount of insoluble Tc in the sludge presents a positive prospect for planning remedial actions related to the sludge.

The amounts of Tc and U dissolved from the sludge by the hydrochloric acid treatments were about 9.2 % and 72 %, respectively (Table 4). Back-titration of the hydrochloric acid treated solutions with sodium hydroxide resulted in reprecipitation of uranium dissolved by the acid treatment. However, the Tc dissolved by the acid treatment not only

**Table 4. Removal of Technetium and Uranium during Acid and Acid/Alkali Titrations**

Treatment	Percent removed	
	$^{99}\text{Tc}$	234,235,238 <sub>U</sub>
HCl (pH 2)	9.2	73
HCl/NaOH (pH 11)	17.1	0.1

**Table 5. Dissolved Ion Concentrations in the Acid and Acid/Alkali Titrated Solutions**

Dissolved cations	HCl treated	HCl/NaOH treated
	mg/L	
Ca	16,000	1850
Mg	650	0.9
K	74	97
Na	53	NA
Si	200	2.7
Al	4800	7.4
Fe	140	0.9

remained in solution during back-titration with the alkali solution, but increased in concentration (Table 4). The hydrochloric acid treatment dissolved the major portion of the sludge, but most of the dissolved alkaline and sesquioxide elements were reprecipitated with uranium after the sodium hydroxide treatment (Table 5).

The dissolution of additional Tc from the acid-treated residues by alkali treatment suggests that some of the Tc in the residue might be in the form of a sulfide compound which could be dissolved through oxidation to sulfate during alkali titration. The technetium sulfide compounds are moderately soluble in alkali solutions under oxidizing conditions.

The experimental results indicate that the remobilization potential of Tc and U in the sludge is low as long as proposed containment methods are able to isolate the sludge from the intrusion of acids and chemical oxidants. However, a significant portion of the sludge, particularly carbonates and sulfates, will be dissolved over the long-term by weakly acidic soil solutions and groundwaters. This dissolution of the sludge should result in a significant volume reduction, which may induce structural instability in the containment. This prediction is based solely on the leaching experiments with the sludge; other factors such as physical and hydrological characteristics and engineering properties of the containment must also be considered in an ultimate remedial action plan.

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